

Evaluation of Amorphous Silicon as a Direct Water Splitting System

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Table of Contents

Abstract	iii.
Introduction	1-2
Methods and Materials	2-4
Results	4-5
Discussion	6-8
Acknowledgements	9
Figures	10-18
References	19

Abstract

Evaluation of Amorphous Silicon as a Direct Water Splitting System. Ken Varner (University of North Carolina at Chapel Hill, Chapel Hill, NC 27514) J. Turner (National Renewable Energy Laboratory, Golden, CO 80401-3393).

Analyses of amorphous silicon (a-Si) electrodes were performed with the goal of creating a monolithic water-splitting device. Different a-Si triple-junction samples were tested with corrosion measurements through current-voltage tests showed that a-SiC protects a-Si in electrolyte solution, but decreases the current density. Also, different metal-ion solutions were applied to the semiconductors by drop-evaporation methods. Tests showed that some of these metal-ion solutions do increase current density. Mott-Schottky measurements showed that our a-SiC samples had a $.75 \Omega^{-1} \Omega$ resistance under illumination. The Band Gaps measured for our a-SiC films were 1.95 eV, 1.93 eV, 1.67 eV, and 1.62 eV. Two standard a-Si triple-junction devices displayed almost no corrosion as well as the highest current density. Further work will be done on these samples with the metal-ion solutions as surface catalysts.

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Introduction

As the world's population grows, causing a direct increase in fossil energy consumption, the environment will experience the heaviest burden. With this, there will probably be strong pressure to reduce CO₂ emissions, causing villages and entire countries to look for solutions in renewable energy technologies. In order for countries to consider these solutions, only systems that contain effective energy storage technology will most likely be considered. Energy storage is especially important with systems that use intermittent resources such as wind and photovoltaics (PV). The production of hydrogen through renewable energy systems will play a key role in attaining a sustainable energy infrastructure (Turner, 1999).

Hydrogen, produced directly from sunlight, can be stored and used as the chemical energy in transportation systems. Currently, PV systems are used to obtain hydrogen from water. The PV panels supply electrical energy to electrolyzers that split the water into H₂ and O₂. However, this approach is commercially expensive. We want to use photoelectrolysis as an advanced and less expensive alternative to the PV-electrolysis system

The photoelectrolysis systems works by using rays of sunlight that strike the surface of a semiconductor within a solution to split water directly on the surface. The primary advantage is that electrical cables and an electrolyzer are no longer needed. Combining an electrolyzer with a simplified PV system eliminates the high capital costs of a full-size hydrogen-producing PV system. A proposed system that will integrate this new technology consists of structures containing water and photoelectric cells placed in

rows on the bottom. The devices can be used with solar trackers in hydrogen-producing farms.

Two issues arise with amorphous silicon's ability to function as a suitable semiconductor for electrolysis: (1) Is the material's bandgap sufficient enough to split water? (2) Is the material stable in aqueous electrolyte solution? As to the first issue, the required voltage for splitting water is 1.6 V. State-of-the-art triple-junction a-Si semiconductors can have voltages greater than 1.8 V. The second issue may be addressed by applying a surface coating of amorphous silicon carbide (a-SiC) as a protective layer for the PV devices. Also, research has shown that by applying transition metal-ions to the surface of the semiconductor can allow electricity to transfer quickly to the water from the semiconductor and prevent surface corrosion (Bansal et al., 2000; Allongue et al., 1984; Kobayashi et al., 1994).

This project's goal is to develop an a-Si-based system that will split water into hydrogen and oxygen through a-Si's direct surface contact with water. This system should split water upon illumination using only sunlight as the energy input. The a-Si samples were characterized to evaluate their potential for water-splitting. The various samples underwent current-voltage tests, corrosion measurements, and metal-ion catalyst treatments. The a-SiC samples were tested for band gaps and resistance.

Materials and Methods

Semiconductor Electrodes

A-Si films (p-i-n solar cells) were deposited on stainless steel substrates via plasma-enhanced chemical vapor deposition (PECVD) with a germane-to-disilane ratio of 0.72.

This ratio is typically used for the i-layer in the bottom cell of the triple-junction cell. Some samples contain heavily doped a-SiC p-layers. These are deposited under the same conditions as a-Si films but their radio frequency (RF) power and deposition times vary with RF power values at 20 W, 50 W, and 160 W and their corresponding deposition times for the p-layer were 3.0 min, 2.5 min, and 1.5 min. Each sample was made into a 2" by 2" wafers, which were then cut into small pieces ($0.02\text{ cm}^2 - 2.2\text{ cm}^2$). We attached the backs of each piece to a copper wire with electrically conductive silver epoxy and then placed it in an oven for over an hour at 80°C . After curing the Ag epoxy, we covered the side and the back of the electrode with a non-conductive epoxy so that only the a-Si's surface ($.02\text{--}.21\text{ cm}^2$) was exposed to the solution.

Chemicals

KOH and concentrated H_2SO_4 were received from J. T. Baker and used as received. Phosphate (pH 7) buffer solution was obtained from Beckman. RhCl_3 , RuCl_3 , and IrO_2 were obtained from Strem and used as received. The metal-ion solutions were made with house deionized water. $.0025\text{ M Ru}^{\text{III}}$ Red was made in pH 1.4 H_2SO_4 solvent.

Metal-ion Treatment

$.010\text{ M RhCl}_3$, and $.010\text{ M RuCl}_3$ solutions were made from dilute HCl solution (pH 2). The metal-ion solutions were deposited onto the electrode surface with a pipette. After 60 s, the electrodes were rinsed with de-ionized water. After immersion in a stream of distilled water, nitrogen was blown across the surface, drying the electrode.

Electrochemical Measurements

Capacitance-voltage (C-V) and Current-voltage (I-V) tests were performed in a conventional three-electrode apparatus with a platinum counter electrode, a saturated

calomel electrode (SCE) as the reference, and the sample as the working electrode. The C-V tests were conducted on a Solartron 1287 Electrochemical Interface and a Solartron 1260 Impedance/Gain-Phase Analyzer in 1 M KOH and 1 M H₂SO₄ solution with a scan range of -1.0 V to +0.7 V. The I-V measurements were conducted on a Voltalab PGZ 301 potentiostat in 1 M KOH, pH 7 buffer, and 1 M H₂SO₄. Different biased potentials were applied to the samples, ranging from -1.5 V to +1.0 V while the current was measured. Also, tests were done with a constant -500 mV applied to the samples over a period of 30 min or 60 min with white light impinging on the surface. These tested experiments tested photocorrosion.

Photocurrent and photon flux measurements were performed with a phase-sensitive technique with a tungsten lamp, light filter, mechanical chopper, monochromator, lock-in amplifier, and potentiostat (Tenne, 1982).

Results

Photocurrent and photon flux, which were used in a-SiC band gap calculations, were measured using an electrochemical setup. A platinum counter electrode, SCE reference electrode, and a-SiC electrode were placed in a 5x10⁻⁴ M Hexaaruthenium solution. The samples were exposed to light ranging from 400 nm to 800 nm while a -.3 V potential was applied. Table 1 shows the band gap values for the various a-SiC samples after plotting (photocurrent / photon flux)^(1/2) vs. photon energy (eV).

Mott-Schottky analyses tested the resistance in a-SiC films. Samples GD498-4 and GD499-4 were tested under .481 W/cm² illumination in 1 M H₂SO₄ solution with Triton X added so that the hydrogen bubbles would not block the surface. Graph 1 and

Graph 2 show the results for this experiment where R is resistance in Ohms and Polarization represents potential in Volts. We are mainly interested in the values at 0 V.

Graph 3 shows the differences in current density and stability within solution among three a-Si triple-junction devices. All samples had RuCl_3 treatment. They were tested under $.481 \text{ W/cm}^2$ for an hour. All three samples were tested in 1 M KOH and then new samples from the same batch were tested in 1 M H_2SO_4 under the same conditions.

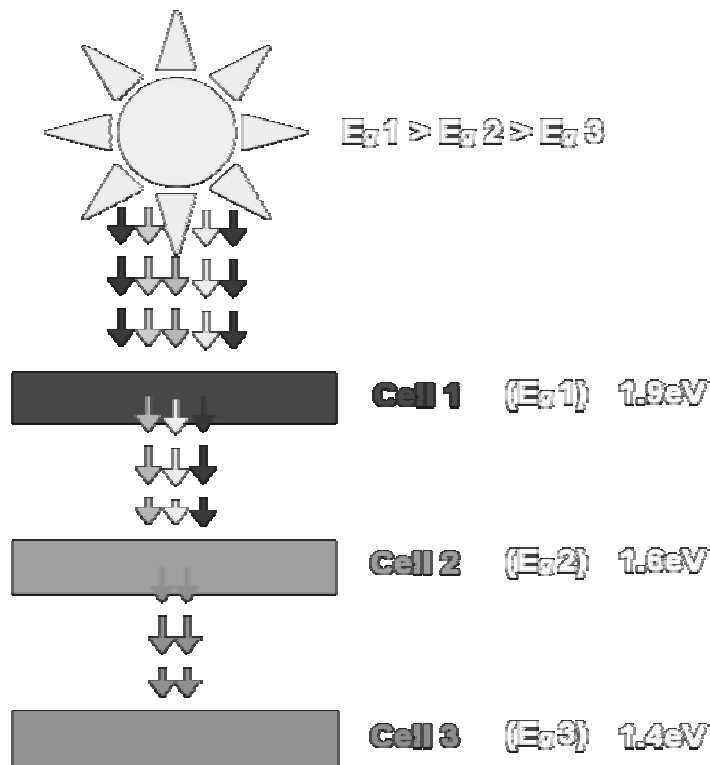
In order to show a comparison of a-SiC's affect when used as a protective layer on a triple-junction a-Si device, a comparison test was done with two triple-junction a-Si devices and two triple-junction a-Si devices with a-SiC deposited on the surface. Graph 4 shows the results these samples under $.481 \text{ W/cm}^2$ illumination with RuCl_3 in 1 M KOH for an hour. Graph 5 shows the samples under the same illumination and metal-ion treatment in 1 M H_2SO_4 .

Testing metal-ion treatments' effects included a look at I-V curves as well as corrosion measurements. Graph 6 shows an a-Si triple-junction device, specifically L3586-4, with various catalysts applied to the surface. The tests were done through cyclic voltammetry in 1 M H_2SO_4 under $.481 \text{ W/cm}^2$ illumination. Graph 7 shows another a-Si triple-junction sample, L3591-4, under the same conditions. The metal-ions' corrosion effects are shown in Graph 8. Sample L3586-4 and L591-4 were in 1 M H_2SO_4 for 30 min under $.481 \text{ W/cm}^2$ illumination. Different catalysts were deposited onto the samples' surfaces.

Discussion

I tested a-SiC to see if it functioned well as a protective layer for the a-Si device. Since the a-SiC film is deposited on the surface of the semiconductor, its physical and optical properties must be optimized to work with the a-Si triple-junction that it protects. Knowing the values for the band gaps is important in the understanding of some of its basic properties. A standard model for an a-Si triple-junction device is shown in Diagram 1. This model was created to enhance the photocurrent as well as minimize the

Diagram 1



This is a Solarex a-Si triple-junction cell with three n-i-p junctions in each cell.*

Obtained from private conversation at NREL. () In our case, for hydrogen production to occur, the junctions are arranged p-i-n.*

photodegradation within the device. Cell 1 absorbs photons with energies from 1.9 eV and above, which then allows Cell 2 to absorb only the energies within the range of 1.6 eV to 1.9 eV. Cell 3 absorbs energies between 1.4 eV to 1.6 eV. The entire visible spectrum is not absorbed in one junction. For a-SiC to be effective in this device without hindering the photocurrent, band gaps in the 2.5 eV range and higher would be ideal. Table 1 shows that two a-SiC samples have band gap values at 1.67 eV and 1.62 eV. This suggests that these films would hinder the photovoltaic process by absorbing the photons that Cell 1 normally absorbs; therefore, causing the device to not function until Cell 2. This would drastically reduce the photocurrent in the system. The films with values of 1.95 eV and 1.93 eV would be better candidates because more light would be allowed to pass through the protective film into the a-Si triple-junction.

As said before, a-SiC's physical properties affect the entire system. Since it is a deposited film on the surface of the electrode, the electrons have to move through the a-SiC. It has a finite thickness, which means that there is resistance. The Mott-Schottky plots shown in Graph 1 and Graph 2 show about .8 Ω in GD498-4 and 1 Ω in GD499-4. Knowing the current output from previous experiments (~15 mV) and the resistance values obtained in Graph 1 and Graph 2, we can use Eq. 1 to determine the decrease in

$$V = I R \quad (1)$$

current density caused by adding 1 Ω to the device. From private conversation with John Turner, I know that a 60 mV decrease in voltage causes a decade decrease in current density. 1 Ω causes a 15 mV decrease in voltage, which drops the current and hydrogen production by a factor of 2.5. This concept could not be tested correctly because we did

not have any non-protected a-Si triple-junctions and a-SiC-protected samples with a-Si triple-junctions that were made under the same parameters as the non-protected, but effectiveness against corrosion was tested. Further studies should include corrosion and I-V tests on samples that are made under the same conditions. Further work should be done on increasing a-SiC's band gap and decreasing the resistance, or possibly integrating the first cell in the device with a-Si and a-SiC.

Graph 4 and Graph 5 compare a-Si triple-junction devices with similar, protected devices. The two samples without the a-SiC protection were chosen from Graph 3 based on relatively high current output with high stability within solution. The only difference in the samples that displayed little corrosion is the production parameters. Graph 4 shows that a-SiC does protect the a-Si device, especially in chemically “aggressive” solutions such as 1 M KOH. When compared in acid, as shown in Graph 5, no noticeable difference occurred between the protected samples vs. the non-protected samples. This suggests that a-SiC may not be necessary to protect the device, especially when the electrolyte solution is water. Tests over a longer period of time should be done to see if there exist long-term corrosion effects.

Some of the metal-ion catalyst solutions did have a positive effect on the electrodes by increasing current density, but none of the solutions affected electrode corrosion. The Iridium solution catalyzed charge the most on sample L3591-4 and Platinum catalyzed the most on L3586-4. Further testing should be done to see which metal-ion solutions catalyze charge transfer the most for an extended period of time.

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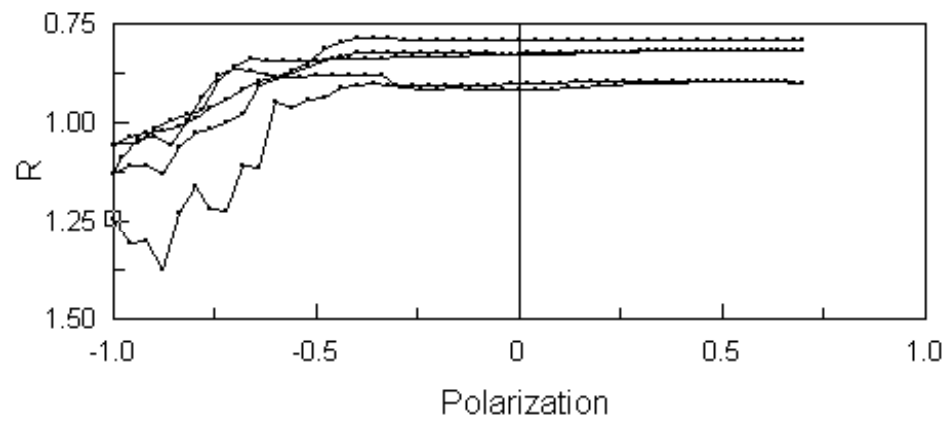
Table 1

Band Gaps for Various a-SiC Films

<u>Sample</u>	<u>Band Gap (eV)</u>
<u>GD498-4</u>	<u>1.95</u>
<u>GD499-4</u>	<u>1.93</u>
<u>SiC113</u>	<u>1.67</u>
<u>SiC114</u>	<u>1.62</u>

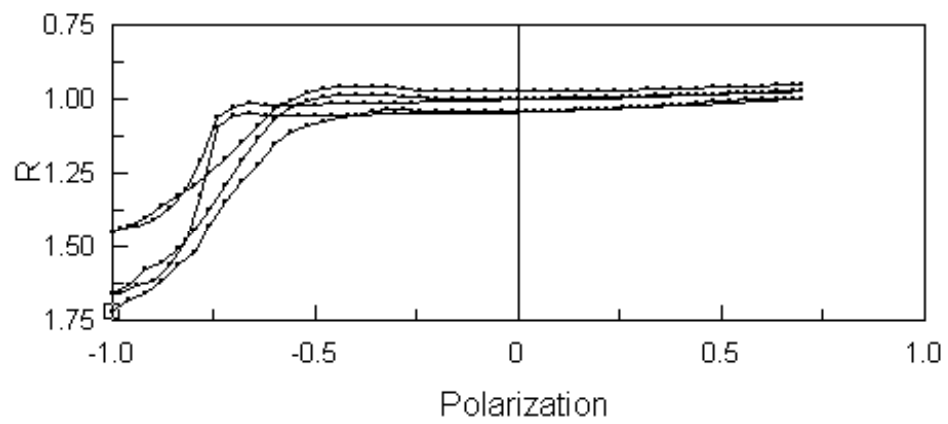
Graph 1

Mott-Schottky Plot for a-SiC Sample GD498-4

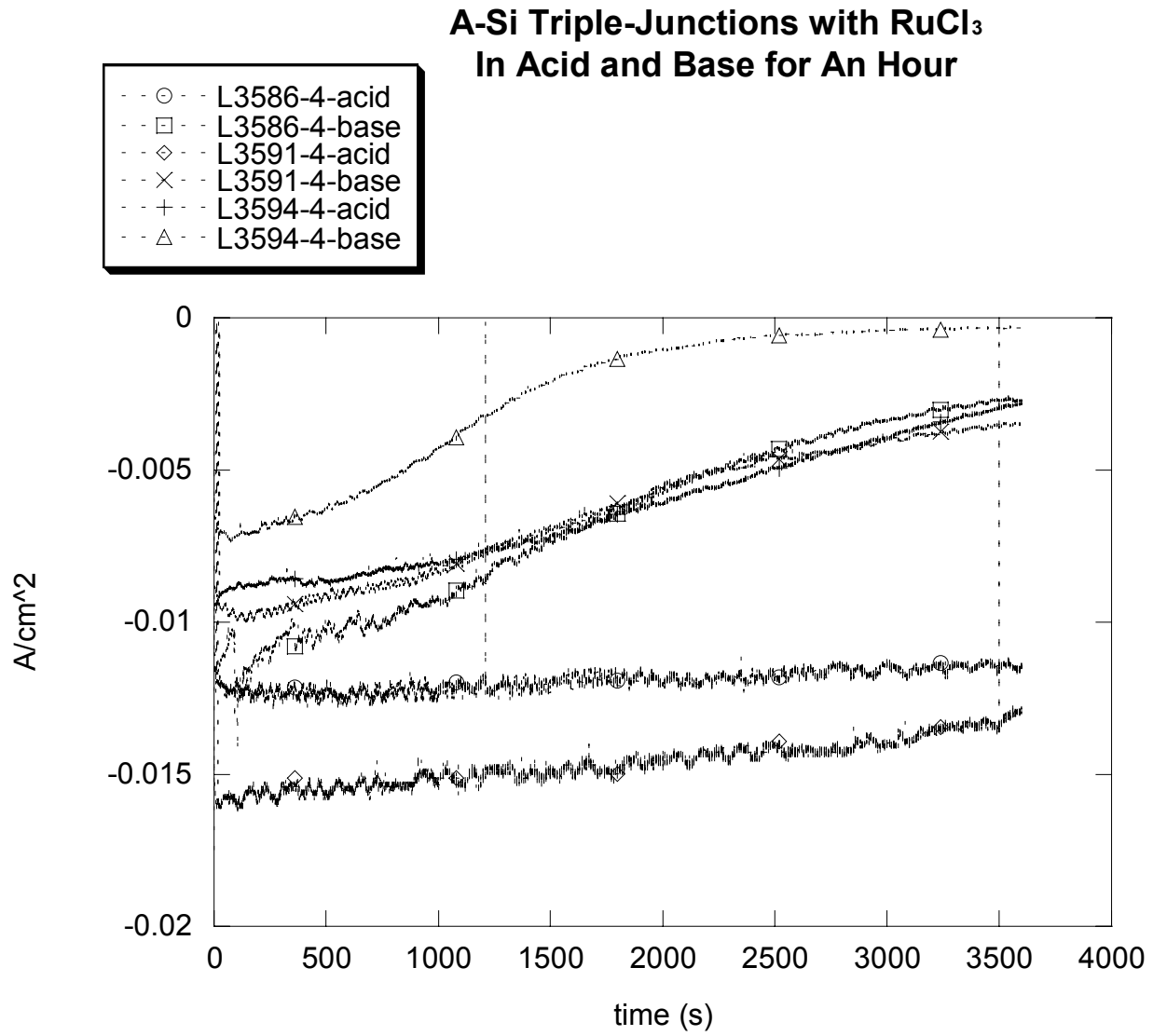


Graph 2

Mott-Schottky Plot for GD499-4

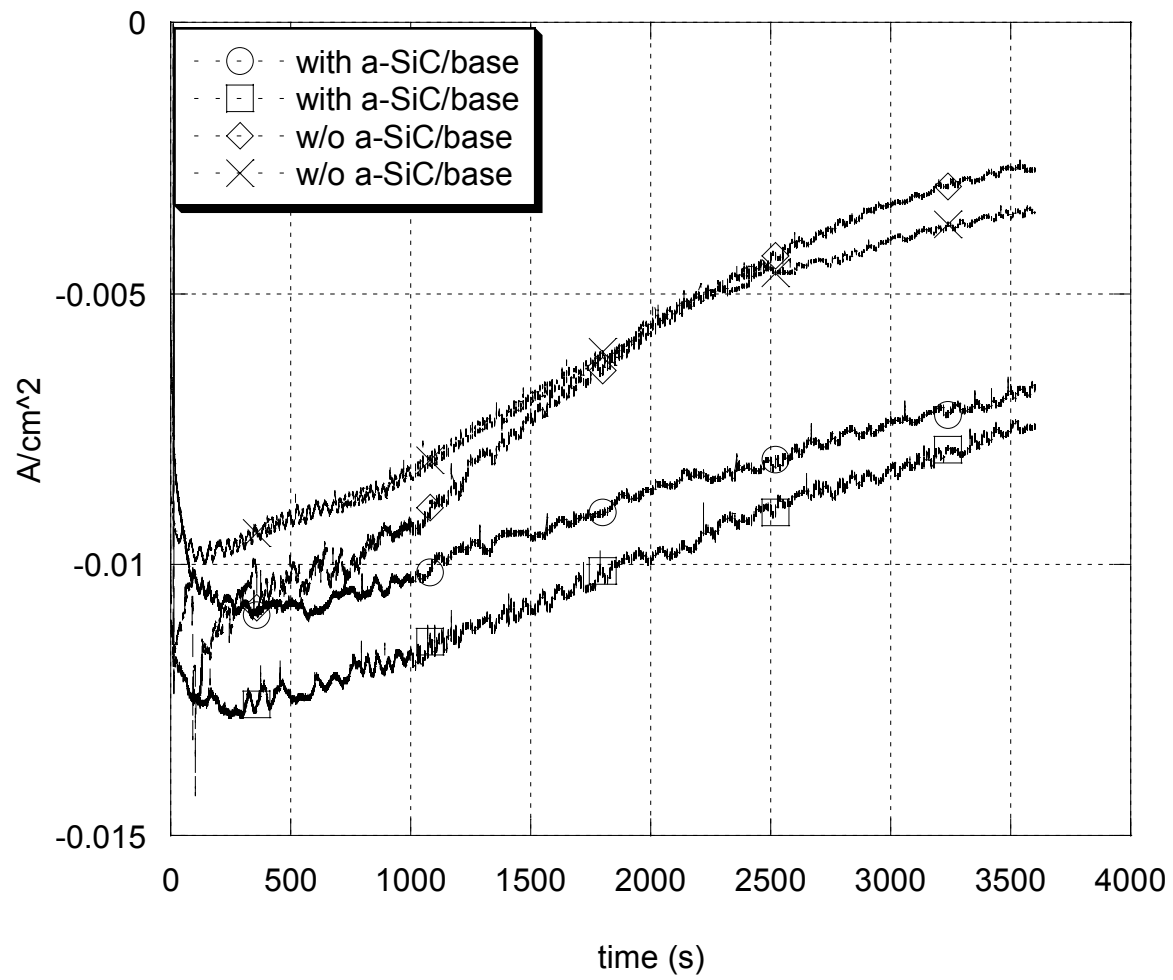


Graph 3



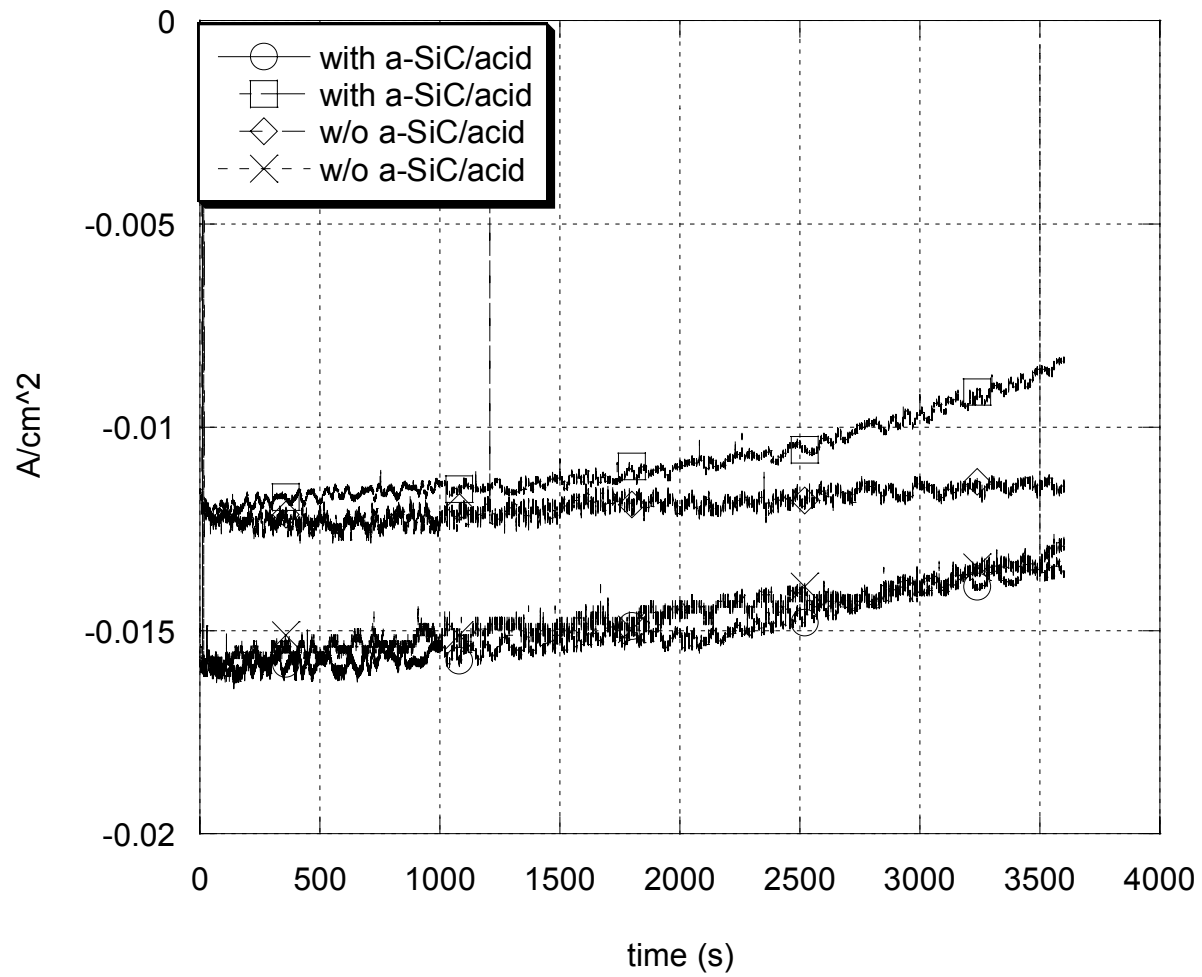
Graph 4

Hour Corrosion of Triple-Junctions with and without
a-SiC In Base with RuCl_3



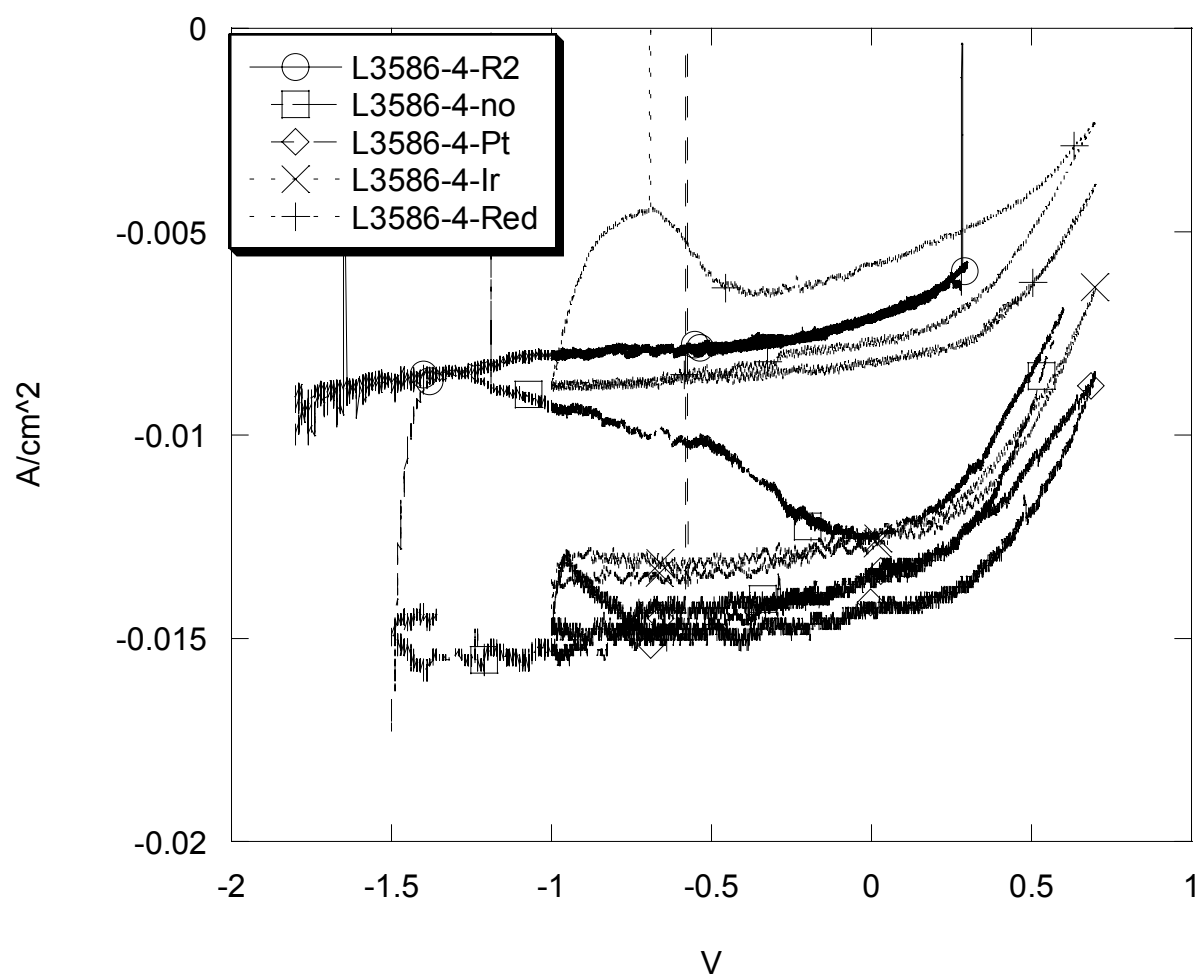
Graph 5

Hour Corrosion of Triple-Junctions with and without
a-SiC in Acid with RuCl_3



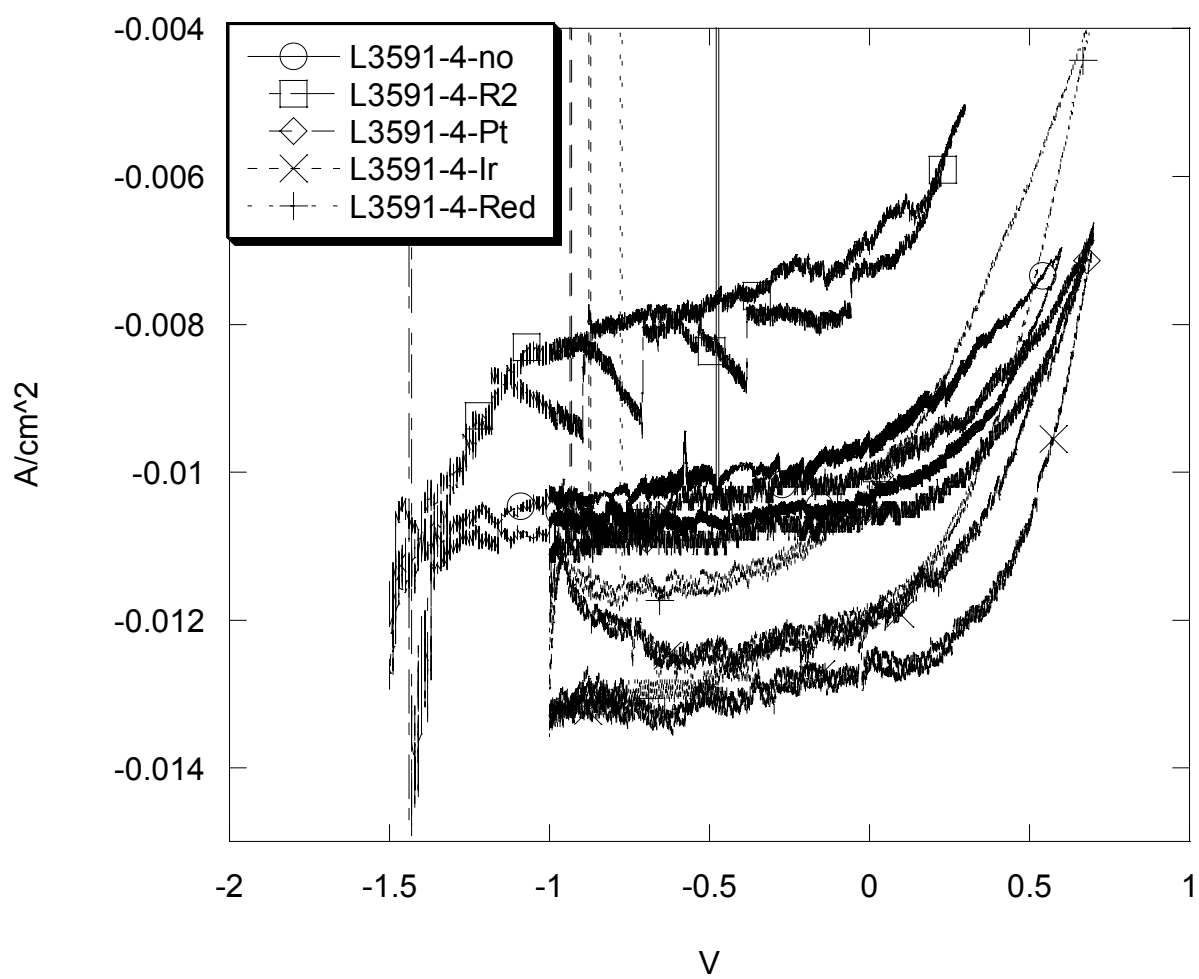
Graph 6

**Different Catalysts on
L3586-4 (w/o a-SiC) in Acid**

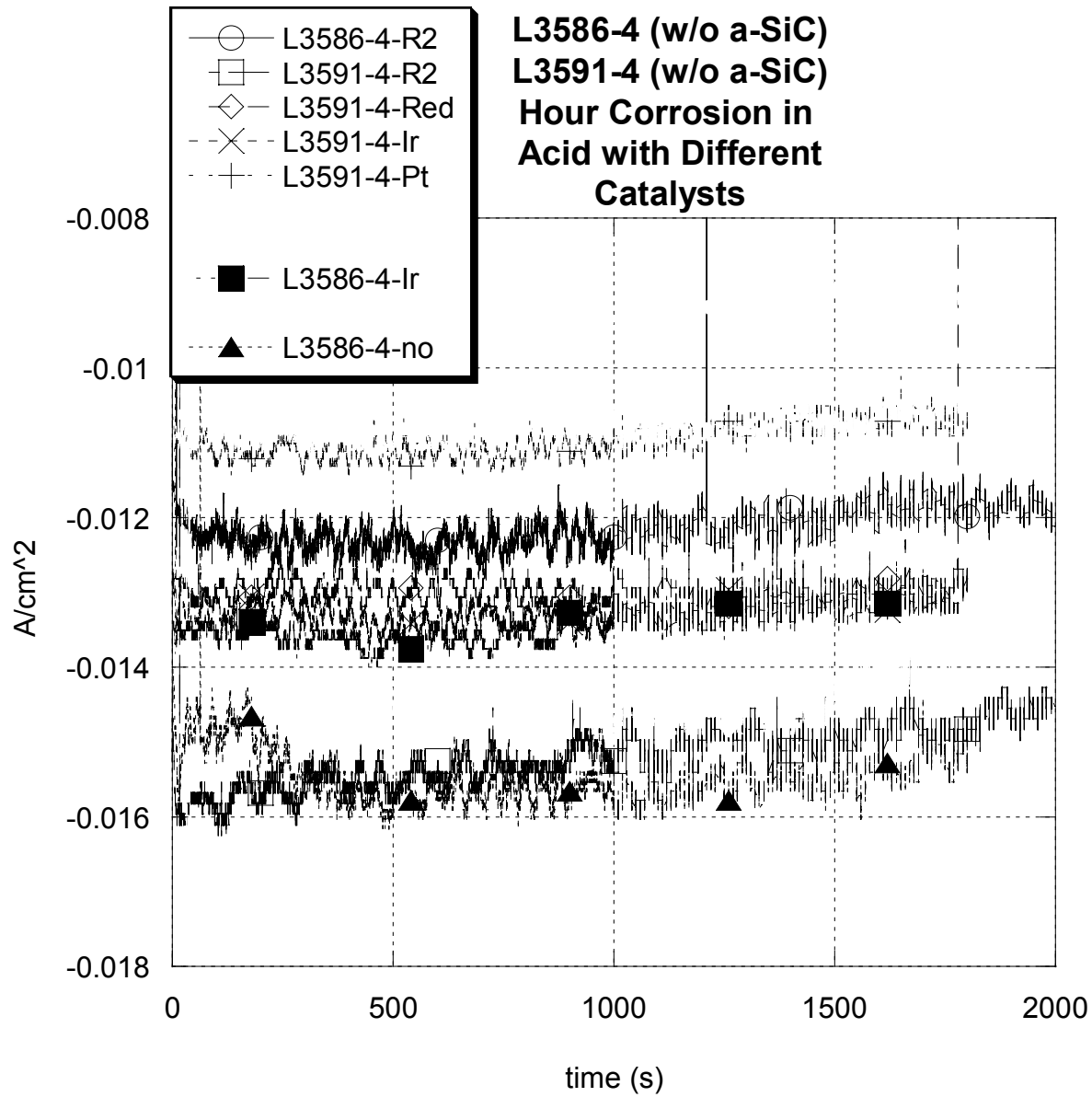


Graph 7

**Different Catalysyts on
L3591-4 (w/o a-SiC) in Acid**



Graph 8



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